



# Recycling of spent nickel–cadmium batteries based on bioleaching process

Nanwen Zhu\*, Lehua Zhang, Chunjie Li, Chunguang Cai

*College of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China*

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## Abstract

Only 1–2 percent of discarded dry batteries are recovered in China. It is necessary to find an economic and environmentally friendly process to recycle dry batteries in this developing country. Bioleaching is one of the few techniques applicable for the recovery of the toxic metals from hazardous spent batteries. Its principle is the microbial production of sulphuric acid and simultaneous leaching of metals. In this study, a system consisting of a bioreactor, settling tank and leaching reactor was developed to leach metals from nickel–cadmium batteries. Indigenous thiobacilli, proliferated by using nutritive elements in sewage sludge and elemental sulphur as substrates, was employed in the bioreactor to produce sulphuric acid. The overflow from the bioreactor was conducted into the settling tank. The supernatant in the settling tank was conducted into the leaching reactor, which contained the anode and cathodic electrodes obtained from nickel–cadmium batteries. The results showed that this system was valid to leach metals from nickel–cadmium batteries, and that the sludge drained from the bottom of the settling tank could satisfy the requirements of environmental protection agencies regarding agricultural use.

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## 1. Introduction

According to the report prepared by the State Environmental Protection Administration of China (SEPA), the quantity of dry batteries produced and consumed has increased rapidly in recent years in China. Peak values were reached in 1998: 14.1 billion batteries were produced and 8.37 billion batteries were consumed (SEPA, 2000). It is estimated that 3.88% of discarded dry batteries are nickel–cadmium batteries. Nickel–cadmium batteries are classified as hazardous waste because nickel and cadmium are heavy metals and suspected carcinogens (Shapek, 1995). However, only 1–2% of discarded dry batteries are recovered in China due to a lack of relevant regulations. Therefore, it is necessary to find an economic and environment friendly process to recycle dry batteries such as nickel–cadmium batteries.

Some methods to treat spent batteries involving pyro and hydrometallurgical techniques, similar to those in the mining industry, have been proven to be quite

expensive or inefficient (Cerruti et al., 1998). The biohydrometallurgical method may be a valuable alternative choice. In the mining industry, the biohydrometallurgical processes have been gradually replacing the hydrometallurgical ones due to their higher efficiency, lower cost and fewer industrial requirements (Ehrlich, 1981; McNulty and Thompson, 1990; Rossi, 1990; Jain and Tygi, 1992; Barret et al., 1993; Cerruti et al., 1998). The biohydrometallurgical process is usually referred to as bioleaching. It is the process by which metals are extracted from ore-bearing rocks using microorganisms (Espejo and Romero, 1987; Norris, 1990). Microorganisms include the chemoautotrophic, acidophilic, and iron- and sulphur-oxidizing bacteria such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* using CO<sub>2</sub> as the sole carbon source and ferrous and reduced inorganic sulphur compounds as the energy source (Norris, 1990). The mechanisms by which microorganisms effect changes in metal speciation and mobility are fundamental components of metal biogeochemical cycles, as well as all other elements including carbon, nitrogen, sulphur, and phosphorous, with additional implications for plant productivity and human health. This unique type of life, very important

\* Corresponding author. Tel.: +86-21-547-42817; fax: +86-21-547-40825.

E-mail address: nwzhu@sjtu.edu.cn (N. Zhu).

from environmental and economic points of view (Gadd, 1999), has been used extensively for metal extraction from low-grade mineral sulphides, and for the removal of metals from sewage sludge (Couillard and Zhu, 1992; Du et al., 1995; Shanableh and Ginige, 1999; Filali-Meknessi et al., 2000; Ito et al., 2000; Xiang et al., 2000; Laberge et al., 2000). In the same way, bio-hydrometallurgy also shows great possibilities in recycling of spent nickel–cadmium batteries preventing the contamination generated by discarded batteries and allowing the recovery of metals in the batteries (Cerruti et al., 1998).

Thiobacilli can grow and produce sulphuric acid using elemental sulphur as the energy source with oxygen as the terminal electron acceptor. This process results in the dissolution of metals including Ni and Cd from broken nickel–cadmium batteries. After the process is complete, the newly detoxified materials can be separated from the liquid (leachate) phase, and the metal will re-precipitate from the metal-laden leachate by raising its pH value (Anderson et al., 1998).

Cerruti has already reported using pure culture of *Thiobacillus ferrooxidans* to dissolve nickel and cadmium from nickel–cadmium batteries. However, the case using indigenous thiobacilli (mixed culture) found in sludge from wastewater treatment plants required further study. It is reported that certain strains of thiobacilli are present in municipal wastewaters, but under normal conditions the low concentration of reduced sulphur compounds does not permit the proliferation of thiobacilli (Blais et al., 1992). However, thiobacilli will grow rapidly with sulphur and oxygen supply.

The objectives of this study were to develop a new method to remove metals from nickel–cadmium batteries using indigenous thiobacilli from sewage sludge and its metabolic product, and meanwhile to clarify the effect of different pH values of sludge on the metal leaching process.

## 2. Material and methods

### 2.1. Sewage sludge sampling

The sewage sludge used was obtained from the primary sludge clarified and secondary activated sludge unit from the Minhang wastewater treatment plant in Shanghai, China. A mixture of primary (65% v/v) and secondary (35% v/v) sludge was used in the experiments. The two sludges were mixed in the same ratio as they were produced in the treatment plant. The mixed sludge was conserved at 4 °C before utilization. The results of the mixed sludge analysis are presented in Table 1.

Table 1  
Characteristics of the tested sludge

pH	Solids	Metals (mg/kg)					
		Cd	Ni	Cr	Cu	Zn	Pb
6.73	2.17	4.2	132.6	9.2	423.6	397.0	8.3

### 2.2. Acclimation of sulphur-oxidizing microflora

A sample of 400 ml of sludge was transferred into a 1000-ml Erlenmeyer flask. One percent (w/v) of powdered elemental sulphur was added and incubated at 30 °C and 200 revolutions per minute (rpm). When the pH value of sewage sludge dropped under 2.0, the initial acclimation was completed. This step took 17 days. Subsequently, another 320 ml of the sludge sample and 1% (w/v) sulphur was mixed in another flask, and 80 ml of acidified sludge from previous acclimating step was inoculated and reincubated under the same conditions. This operation was repeated successively until the rate of pH reduction to 2.0 was maximized over two consecutive transfers. When the maximum rate appeared, the indigenous sulphur-oxidizing bacteria were assumed to be adapted (Blais et al., 1992). This is the final acidified sludge.

### 2.3. Leaching system and its operation

Experiments were conducted at 30 °C in a reactor system. The system was mainly consisted of two reactors, i.e. bioreactor and leaching reactor (Fig. 1). The bioreactor was used to culture indigenous thiobacilli in sewage sludge, and produced sulphuric acid through oxidation of sulphur. The leaching reactor was used to leach metals from spent batteries. The volumes of the bioreactor and the leaching reactor were 2.43 and 1.65 l, respectively.

A sludge sample of 800 ml maintained in the refrigerator at 4 °C was transferred into the bioreactor and mixed with 200 ml of the final acidified sludge (see Section 2.2). One percent (w/v) of elemental sulphur was added. Then, a flow of fresh sewage sludge mixed with 1% powdered sulphur was continuously fed to the bioreactor, and

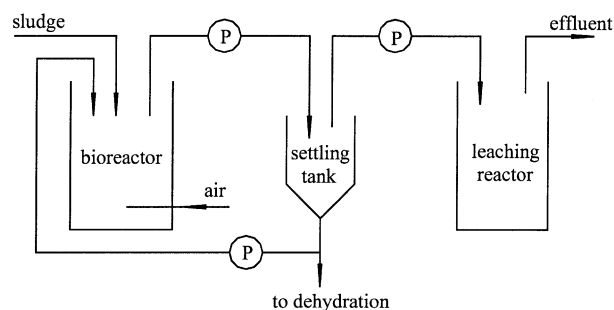


Fig. 1. Schematic diagram of the metals leaching process.

a flow of fresh air was supplied with an air diffuser that was controlled manually through a regulator. To ensure the proliferation and activity of acidophilic thiobacilli, a high level dissolved oxygen concentration (about 3.0 mg/l) was maintained. The bioreactor operated at a fixed level with overflow going to the settling tank. The acidified sludge from the bioreactor was thickened in the settling tank, and part of the thickened sludge (20%) was recycled to the bioreactor. The effluent from the settling tank was conducted into the leaching reactor which contained anodic and cathodic material obtained from nickel–cadmium batteries. The pH value and metal concentrations of the effluent were determined before entering the leaching reactor. During the leaching process, the metal concentration of the solution flowing from leaching reactor was also determined.

Anodic and cathodic material containing different concentrations of nickel and cadmium were recovered from three pairs of spent nickel–cadmium batteries with the same brand. Three samples consisting of the same component were made. Each sample contained 9.3 g anodic and 9.1 g cathodic materials, which include 2.34 g cadmium and 6.23 g nickel. The leaching effect of each sample at different residence times of the sludge in bioreactor (RTB) was tested.

The experiment included two steps. The first step was to clarify the relationship between RTB and the pH value of the settling tank supernatant. The second step was to determine the effect of leaching metal from the electrodes of nickel–cadmium batteries.

#### 2.4. Analysis method

The sludge pH was measured by a pH meter (Mettler Toledo 320-S). After the start of the first step (see Section 2.3), 50 ml of settling tank supernatant was sampled each day to determine the pH and the concentrations of heavy metals including Cd, Ni, Cr, Cu, Zn, Pb. When the second step began, 15 ml of leaching reactor effluent was extracted to determine the nickel and cadmium concentrations by plasma emission spectrometry (ICP, Iris Advantage 1000).

### 3. Results and discussion

#### 3.1. Bioreactor assay

The pH value and metal concentrations of the effluent from the setting tank at different RTB are presented in Table 2. The acidophilic thiobacilli populations in the bioreactor are also shown. At all RTBs (1, 2, 3, 4, 5, and 6 days), the bioreactor achieved a steady state after a transition period. The steady state was maintained continuously for 4 days. The data in Table 2 present an average value of three samples taken during the steady

Table 2

Variation of pH, metal concentration, and thiobacilli population with different RTB

RTB (day)	pH	Metals concentration (mg/l)		Thiobacilli (cfu/ml)
		Cd	Ni	
6	1.81	0.0738	2.0593	$4.6 \times 10^7$
5	1.88	0.0673	1.9356	$6.7 \times 10^7$
4	1.86	0.0651	1.8163	$2.8 \times 10^7$
3	1.97	0.0564	1.5624	$2.0 \times 10^7$
2	2.25	0.0434	1.4930	$3.2 \times 10^6$
1	2.93	0.0347	1.3237	$6.0 \times 10^6$

state. The pH value, the metal concentrations of the overflow and the population of acidophilic thiobacilli in acidified sludge were very similar when the RTB was above 4 days. The pH value increased from 4 to 1 day RTB, but the metal concentrations and the thiobacilli population decreased. It is very clear that the acidification of the sludge is due to the oxidation of sulphur by thiobacilli (Couillard and Zhu, 1991), and the solubilities of metals in sludge have strong relationship to the pH value (Du et al., 1995). The sulphur was first converted to colloidal sulphur and then oxidized to sulphuric acid which maintained a low pH value (Karavaiko et al., 1988). Thiobacilli proliferated in this process, and its population increased with increasing RTB when the nutritive elements in sludge and elemental sulphur were stable enough for thiobacilli proliferation and the pH value was still not so low as to prevent its activity.

#### 3.2. Solid–liquid separation

The solid sludge from the bioreactor was separated from the liquid in the settling tank. To maintain the same state of solid–liquid separation, a 1 h retention time was maintained for every case. If the settling time was <45 min, the separation process was not sufficient. The supernatant from the settling tank was conducted into the leaching reactor.

The supernatant contained colloidal sulphur converted from elemental sulphur and thiobacilli from the acidified sludge. The population of acidophilic thiobacilli in the supernatant was still high, although lower than that in the acidified sludge (data not shown). The metal concentrations in the sludge that was drained from the bottom of settling tank could be calculated from the data presented in Tables 1 and 2. Table 3 shows the results of metals removal from sludge at different RTB. According to the Control Standard for Pollutants in Sludges for Agricultural Use (GB4284-84), the drained sludge could be applied to agricultural land. The supernatant obtained from the settling tank was used for the metal solubilization.

Table 3  
Results for metals removal from sludge at different RTB

Metals contained in sludge	Removal required (%)	Metals removed (%) at different RTB (day)					
		6	5	4	3	2	1
Cd	–	81.7	74.5	71.2	61.4	47.1	38.9
Ni	24.6	71.6	67.3	63.1	54.3	51.9	41.6
Cr	–	61.5	57.1	56.2	47.3	36.4	31.1
Cu	41.0	96.1	94.3	90.4	87.5	83.6	78.1
Zn	–	94.6	91.7	89.1	83.2	78.1	71.1
Pb	–	48.5	44.1	41.7	31.4	24.7	11.5

### 3.3. Metal leaching

Now that a low pH in solution (the supernatant overflowed from the settling tank) is necessary for metal leaching, and the less solution used, the less equipment capacity needed, leaching experiments were carried out at 3, 4, and 5 days RTB. The duration of the experiments was 50 days.

The supernatant obtained from the settling tank was transferred into the leaching reactor. The hydraulic retention time (HRT) for each case was maintained constant (24 h). The overflow from the leaching reactor was collected and analyzed at 5-day intervals. The nickel and the cadmium concentrations at different sludge RTBs (3, 4, 5 days) in the bioreactor are presented in Figs. 2 and 3, respectively.

Fig. 2 shows that the cadmium concentration in the overflow remained relatively stable during the first 15 days in the case of 5 and 4 days RTBs, increased during the following 10 days, and then decreased rapidly. At a residence time of 3 days, however, the cadmium concentration in the overflow increased during the first 24 days, and then decreased. When the cadmium concentration in the overflow approached that in the inflow

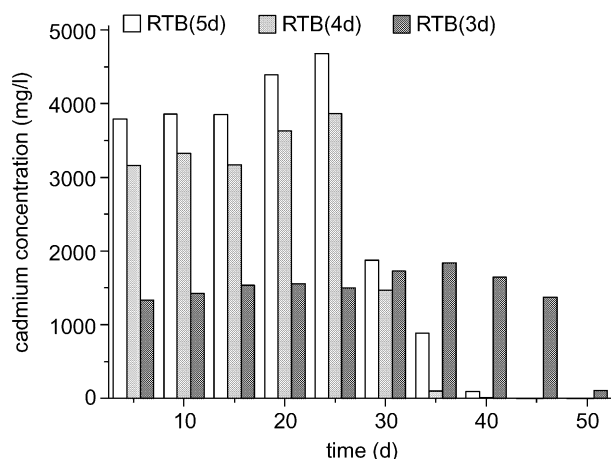


Fig. 2. Change of cadmium concentration in the overflow during the bioleaching process at different RTB (the residence time of the sludge in bioreactor).

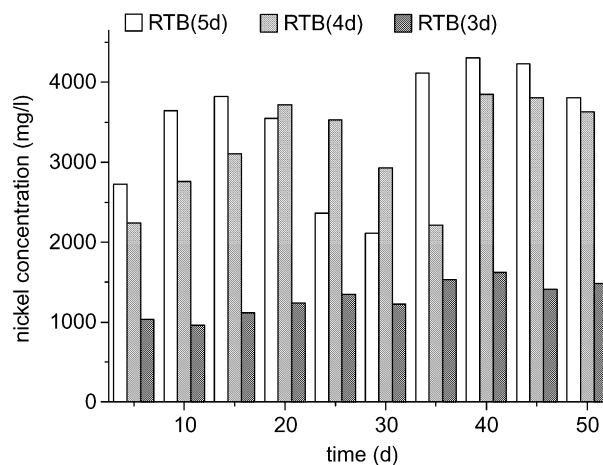


Fig. 3. Change of nickel concentration in the overflow during bioleaching process at different RTB (the residence time of the sludge in bioreactor).

(the supernatant of the settling tank), it was concluded that all of the cadmium in the electrodes had been released.

Changes in the nickel concentration in the overflow are shown in Fig. 3. At the residence time of 5 days (RTB), the nickel concentration in the overflow increased during the first 10 days, then remained relatively stable in the following 10 days, but decreased in the next 10 days. The phenomenon repeated in the following days. At the residence time of 4 days, the nickel concentration in the overflow increased during the first 10 days, then remained stable in the following 5 days. After that, the increase and decrease occurred alternatively. At the residence time of 3 days, the nickel concentration was stable during the first 15 days, increased in the next 12 days, and then decreased.

It was clear that the metal concentrations in the effluent (from the bioleaching tank) increased with the RTBs during the first 30 days for cadmium and the first 40 days for nickel. The difference of concentration for each case may be a result of the different actual HRT for one unit supernatant in the leaching reactor. The cause of the increase and decrease of the metal concentration in the leaching process remains unclear. However, it was possible to conclude that the increases and decreases were a balance of the actions of acid, bacteria, and intermediate compounds produced in the process of sulphur oxidation, and the changing exposed surface. Initially, the bacteria activity was inhibited by metals at high concentrations, and the acid leaching was a single factor of metal dissolution. As time went by, the thio-bacilli adapted to the high metal concentrations and attacked the metals, which exposed surfaces of the electrode enlarged with the metal dissolution, and therefore the leaching rate tended to increase. However, when the leaching process continued, the metal dissolution rate decreased because the high bacteria population could



Table 4  
Summary of the results of total metals dissolution at different RTB

RTB day	Total metals dissolved (mg)		Contribution of sludge (mg)		Total solution (l)
	Cd	Ni	Cd	Ni	
5	2341.4	3467.8	0.67	19.36	10.0
4	2341.4	3974.4	0.81	22.70	12.5
3	2340.1	2162.0	0.94	26.09	16.7

attach to the metals and a low bacteria population could attach to sulphur (or colloidal sulphur) and catalyze its oxidation producing leaching medium (Curutchet et al., 1990; Cerruti et al., 1998).

The thiobacilli attacking the cadmium turned to attack nickel when almost all of the cadmium was released into the solutions; therefore, the dissolution of nickel increased. However, the nickel concentration decreased again with time, the variation trends seem similar to that of cadmium concentration.

The metal dissolution had a similar behavior in each case. Nickel released more slowly than cadmium did. It may be due to the higher solubility of cadmium hydroxide than nickel hydroxide and the higher reducing power of cadmium than nickel, i.e. elemental cadmium is more easily oxidized than elemental nickel (Cerruti et al., 1998). The attack of cadmium by bacteria was faster than that corresponding to nickel.

The total dissolution of cadmium and nickel during the 50 days is presented in Table 4. According to the calculations based on the concentration in the leaching reactor effluent, release of all of the cadmium only requires 40 days at 5 days RTB, 35 days at 4 days RTB, and 50 days at 3 days RTB. However, the total nickel recovered during the 50 days was only 66.1, 75.6 and 40.8% for the RTB of 5, 4, and 3 days, respectively.

Therefore, the metal leaching is most effective at a residence time of 4 days. The total amount of solution (sludge) is 10.0 l at 5 days RTB, 12.5 l at 4 days RTB, and 16.7 l at 3 days RTB.

#### 4. Conclusions

The research demonstrated that using sewage sludge as the thiobacilli source and elemental sulphur as an energy source could produce sulphuric acid and reducing-power compounds effectively. The products were useful to leach metals from electrodes of nickel–cadmium batteries. The following conclusions can be drawn from the foregoing research:

1. The pH value, the metal concentrations of the overflow and the population of acidophilic thiobacilli in acidified sludge changed with the different RTB. The pH value increased from 4 to 1

day RTB, but the metal concentrations and the thiobacilli population decreased. However, the data were very similar when the RTB was above 4 days. In the case of 4–6 days RTB, the pH value was 1.81–1.88, and at 1 d RTB the pH value was 2.93.

2. A higher metal concentration in effluent occurred with a longer RTB during the leaching process (the metal concentration at 5 days RTB was more three times than that at 3 days RTB). However, due to the different total amount of solution used in each case, the metal leaching efficiency did not change based on the RTB only.
3. All of the cadmium could be released during the 50 days' leaching experiment, but the total nickel recovered during the 50 days was only 66.1, 75.6, and 40.8% for the RTB of 5, 4, and 3 days, respectively. Therefore, metal leaching is most effective at the RTB of 4 days.
4. Sludge drained from the settling tank meets the requirements of environmental protection agencies regarding agricultural application. It can be applied to agricultural land after neutralized by lime.

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#### References

- Anderson, B.C., Brown, A.T.F., Watt, W.E., Marselek, J., 1998. Biological leaching of trace metals from stormwater sediments: influential variables and continuous reactor operation. 38(10), 73–81.
- Barret, J., Hughes, M.N., Karavaiko, G.I., Spencer, P.A., 1993. Metal Extraction by Bacterial Oxidation of Minerals. Ellis Horwood, Chichester.
- Blais, J.K., Tyagi, R.D., Auclair, J.C., 1992. Bioleaching of metals from sewage sludge by sulfur-oxidizing bacteria. Journal of Environmental Engineering 118 (5), 690–707.
- Cerruti, C., Curutchet, G., Donati, E., 1998. Bio-dissolution of spent nickel–cadmium batteries using *Thiobacillus ferrooxidans*. Journal of Biotechnology 62, 209–219.
- Couillard, D., Zhu, Shucai, 1992. Bacterial leaching of heavy metals from sewage sludge for agricultural application. Water, Air and Soil Pollution 63, 67–80.
- Curutchet, G., Donati, E., Tedesco, P., 1990. Influence of quartz in the bioleaching of covellite. Biorecovery 2, 19–25.
- Department of Rural and Urban Construction and Environmental Protection, 1984. Control Standards for Pollutants in Sludges from Agricultural Use. GB4284-84.
- Du, Y.G., Tyagi, R.D., Sreekrishnan, T.R., 1995. Operation strategy for metal bioleaching based on pH measurements. Journal of Environmental Engineering 121 (7), 527–535.
- Ehrlich, H.L., 1981. Geomicrobiology. Marcel Dekker De, New York.

- Espejo, R.T., Romero, P., 1987. Growth of *Thiobacillus ferrooxidans* on elemental sulfur. *Applied Environmental Microbiology* 53, 1907–1912.
- Filali-Meknessi, Y., Tyagi, R.D., Narasiah, K.S., 2000. Simultaneous sewage sludge digestion and metal leaching: effect of aeration. *Process Biochemistry* 36, 263–273.
- Gadd, G.M., 1999. Fungal production of citric and oxalic acid: importance in metal speciation, physiology and biogeochemical processes. *Adv. Microb. Physiol* 41, 47–92.
- Ayumi, Ito, Umita, Teruyuki, Aizawa, Jiro, 2000. Removal of heavy metals from anaerobically digested sewage sludge by a new chemical method using ferric sulfate. *Water Research* 34 (3), :751–758.
- Jain, D. K., Taygi, R.D., 1992. Leaching of heavy metals from anaerobic sewage sludge by sulfur-oxidizing bacteria. *Enzyme Microb. Technol* 14, 376–383.
- Karayaiko, G., Rossi, G., Agate, A., Groudev, S., Avakyan, Z., 1988. *Biogeotechnology of Metals*. Centre for International Projects GKNT, Moscow.
- Laberge, Claude, Cluis, Daniel, Mercier, Guy, 2000. Metal bioleaching prediction in continuous processing of municipal sewage with *Thiobacillus Ferrooxidans* using neutral networks. *Water Research* 34 (4), 1145–1156.
- McNulty, T.P., Thompson, D.L., 1990. Economics of bioleaching. In: Ehrlich, H.L., Brierley, C.L. (Eds.), *Microbial Mineral Recovery*. McGraw-Hill, New York.
- Norris, P.R., 1990. Acidophilic bacteria and their activity in mineral sulfide oxidation. In: Ehrlich, H.L., Brierley, C.L. (Eds.), *Microbial Mineral Recovery*. McGraw-Hill, New York.
- Rossi, G., 1990. *Biohydrometallurgy*. McGraw-Hill, Hamburg.
- SEPA, 2000. Policy for recycling spent batteries will be established. *Environmental and Healthy Engineering* 8 (1), 6.
- Shanableh, Abdallah, Ginige, Pushpa, 1999. Impact of metals bioleaching on the nutrient removal biosolids. *Water Science and Technology* 39 (6), 175–181.
- Shapek, R.A., 1995. Local government household battery collection program: costs and benefits. *Resour. Conserv. Recycl* 15, 1–19.
- Xiang, L., Chan, L.C., Wong, J.W.C., 2000. Removal of heavy metals from anaerobically digested sewage sludge by isolated indigenous iron-oxidizing bacteria. *Chemosphere* 41 (1–2), 283–287.